

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 03-208900

(43)Date of publication of application :12.09.1991

(51)Int.Cl.

C30B 33/10

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(54) WASHING METHOD FOR SILICON WAFER

(57)Abstract:

PURPOSE: To obtain a silicon wafer having high cleanliness by washing this silicon wafer by using an aq. soln. contg. hydrogen fluoride and contg. a specific oxidizing agent as a detergent.

CONSTITUTION: The aq. soln. contg. 0.1 to 20wt.% hydrogen fluoride and contg. the oxidizing agent described below as the detergent is used at the time of washing the silicon wafer. (i) 0.5 to 25wt.% sulfuric acid or (ii) 0.05 to 10wt.% hydrogen peroxide or (iii) bubbles of an oxidative gas are used as the above mentioned oxidizing agent. Gases contg. oxygen and nitrogen suboxide are usable as the oxidizing gas. Ultrapure water is used as the solvent. The evaporation of the hydrogen fluoride and the water and the evaporation decomposition of nitric acid are accelerated and the compsn. of the washing liquid may deviate from the range of this method if the washing temp. is increased to more than a necessary high temp. Further, the heating up takes time and such may drastically impair workability and, therefore, the heating up to 80°C is more preferable.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's
decision of rejection]

[Date of requesting appeal against
examiner's decision of rejection]

[Date of extinction of right]

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③ 日本国特許庁(JP)

⑩ 特許出願公開

② 公開特許公報(A) 平3-208900

⑤ Int. Cl.³
C 30 B 33/10識別記号 庁内整理番号
7158-4G

④ 公開 平成3年(1991)9月12日

審査請求 未請求 請求項の数 3 (全6頁)

⑥ 発明の名称 シリコンウェハの洗浄方法

⑦ 特 願 平2-3386

⑧ 出 願 平2(1990)1月12日

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明 細 書

1. 発明の名称

シリコンウェハの洗浄方法

2. 特許請求の範囲

(1) シリコンウェハを洗浄するに際し、0.1～20重量%の弗化水素を含有し、かつ酸化剤として、0.5～25重量%の硝酸を含有する水溶液を洗浄液とすることを特徴とするシリコンウェハの洗浄方法。

(2) シリコンウェハを洗浄するに際し、0.05～10重量%の弗化水素を含有し、かつ酸化剤として0.05～10重量%の過酸化水素を含有する水溶液を洗浄液とすることを特徴とするシリコンウェハの洗浄方法。

(3) シリコンウェハを洗浄するに際し、0.05～10重量%の弗化水素を含有し、かつ酸化剤として酸化性ガスの気泡を混入せしめた水溶液を洗浄液とすることを特徴とするシリコンウェハの洗浄方法。

3. 発明の詳細な説明

産業上の利用分野

本発明は、シリコンウェハの表面を高洗浄な状態にするための洗浄方法に関するものである。

従来の技術

近年、デバイスの高集積化に伴って、その基盤となるシリコンウェハの表面をより一層高純化することが強く望まれている。

シリコンウェハの表面に、シリコン粒子や酸等の微粒子汚染物質(パーティクルとも呼ばれる)が存在すると、デバイス配線の断線やショートの原因となり、遷移金属等の金属系汚染物質があると、酸化誘起遅延欠陥の発生やライフタイムの低下といった問題が生じる。このため、これら汚染物質を除去するための洗浄が行われるが、洗浄の際に汚染されることも避けなければならない。

従来のシリコンウェハの洗浄方法としては、

① 希弗酸水溶液で洗浄する方法、② 塩酸または硝酸と過酸化水素との混合水溶液で洗浄する方法、および③ アンモニアと過酸化水素の混合水溶液で洗浄する方法が行われている。これらも洗浄法で

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使用される洗浄液には、微粒子汚染物質や金属系汚染物質を極力低減した高純度の薬品類や水が使用されている。

従来の洗浄方法のうち、①はシリコンウェハ表面に通常10μm程度の厚さで存在する自然酸化膜を溶解する能力を有し、酸化膜中の金属系汚染物質の除去効果は高いが、微粒子汚染物質の低減は難しいという問題がある。

②は塩酸または硝酸が持つ金属系汚染物質に対する溶解能力を利用したものであるが、酸化膜を溶解する能力がない。このため、酸化膜上の金属系汚染物質を除去する効果は高いが、酸化膜中や酸化膜とシリコンの界面に存在する金属系汚染物質を除去する効果は低い。

③はシリコン自身を溶解する働きがあるため、その上に存在する金属系汚染物質を除去する効果は高いが、塩基性の洗浄液中で生成する酸化膜は洗浄液中の金属系汚染物質等を取り込み易いという性質があり、シリコンウェハが再汚染される可能性が高い。しかし、この方法は微粒子の除去効

したがって、スライトエッチ法でもシリコンウェハの高純浄化には限界があると言わざるを得ない。

発明が解決しようとする課題

シリコンウェハ表面の汚染度を評価する方法の一つに、マイクロ波反射法によるライフタイム（以下、再結合ライフタイムという）を調べる方法がある。本発明者は、この方法を用いて、各種方法により洗浄したシリコンウェハの汚染度を評価した結果、アンモニアと過酸化水素の混合水溶液を用いる洗浄で洗浄液中にFeが含まれている場合は、Fe量が0.5ppbという極微量存在しても 8×10^{11} steps/cm²程度のシリコンウェハ表面に付着して汚染し、再結合ライフタイムが低下するといった問題を起こすことがわかった（大塚ら、第34回半導体・集積回路技術シンポジウム予稿集、1988年、P.97）。

本発明は、シリコンウェハを洗浄するに際して、Fe等の金属系汚染物質および微粒子汚染物質を極めて低減し、酸化誘起膜層欠陥の発生やライ

エが高いため、ウェハメーカーやデバイスメーカーで広く利用されている。

また、上記従来法の問題点を解消する方法として、60重量%の硝酸と0.1重量%以下の弗化水素の混合水溶液中にシリコンウェハを浸漬して洗浄するスライトエッチ法と呼ばれる方法が提案されている。（Sitoo Takizawa 他、"Extended Abstracts of Solid State Devices and Materials", 1988年、P.475）。

しかし、半導体用グレードと呼ばれる最高純度の硝酸でも、ppbオーダーまたはサブppbオーダーの金属系汚染物質たとえばAl、Cu、Fe、K、Na、Zn等が含まれているので、60重量%もの高濃度の硝酸を含む洗浄液中の金属系汚染物質の濃度は高く、また石英ガラス製の洗浄槽を使用すると石英ガラス中の金属不純物が溶出して、その濃度はますます高まる。

そして、高濃度の硝酸の強い酸化力でシリコンウェハの表面に酸化膜が形成され、洗浄液中の金属系汚染物質が酸化膜中に取り込まれ易くなる。

ライフタイムの低下といった品質問題がなく、かつデバイスにした場合の電気特性の劣化もない高純度のシリコンウェハを得ることを目的とする。

課題を解決するための手段および作用

本発明の要旨はつぎのとおりである。

- (1) シリコンウェハを洗浄するに際し、0.1~20重量%の弗化水素を含有し、かつ酸化剤として0.5~25重量%の硝酸を含有する水溶液を洗浄液とすることを特徴とするシリコンウェハの洗浄方法。
- (2) シリコンウェハを洗浄するに際し、0.65~10重量%の弗化水素を含有し、かつ酸化剤として0.65~10重量%の過酸化水素を含有する水溶液を洗浄液とすることを特徴とするシリコンウェハの洗浄方法。
- (3) シリコンウェハを洗浄するに際し、0.05~10重量%の弗化水素を含有し、かつ酸化剤として酸化性ガスの気泡を混入せしめた水溶液を洗浄液とすることを特徴とするシリコンウェハの洗浄方法。

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本発明法は、シリコンウェハを洗浄するに際し、洗浄液中の不純物を極力低減するために薬剤の添加量を最小限に抑え、しかも洗浄能力に優れた液を使用する。すなわち、本発明法は、必要最小限の弗素イオンを含む強酸性の水溶液に酸化剤を加えて、シリコンウェハ表面の酸化膜を溶解するとともにシリコンに対するエッチング能力をもたせることにより、 Pb 等の金属系汚染物質を効果的に除去するものであり、酸化剤として、請求項(1)においては必要最小限の硝酸を使用し、請求項(2)においては必要最小限の過酸化水素を使用し、請求項(3)においては酸化性ガスを使用する。

本発明法において、洗浄液中の弗化水素、硝酸および過酸化水素の濃度は、それぞれ HF 、 HNO_3 、および H_2O_2 としての重量%である。請求項(3)においては、酸化性ガスとして酸素および亜酸化窒素（一酸化二窒素）等を含むガスを使用することができる。また、溶媒としては超純水を使用する。

濃度かつ過酸化水素が0.05重量%未満だと、金属系汚染物質の除去効果が不十分である。弗化水素の濃度を増して10重量%を超えると、シリコンウェハの表面に微粒子汚染物質が増加する傾向が認められる。また過酸化水素の濃度を増して10重量%を超えると、シリコン表面のエッチング量が過大になってウェハ表面が荒れて劣った状態になる。そして、弗化水素が10重量%以下でかつ過酸化水素が10重量%以下では、薬剤から混入する不純物の濃度は実質上問題ない。

したがって、弗化水素の濃度を0.05～10重量%、過酸化水素の濃度を0.05～10重量%とした。なお、洗浄温度については、80℃を超えると洗浄むらが生じて熱処理後のシリコンウェハ表面にピット状欠陥を誘起するおそれがあるので、80℃以下とするのが望ましい。

請求項(3)において、弗化水素が0.05重量%未満でかつ酸化性ガスの気泡を混入させない場合は金属系汚染物質の除去効果が不十分である。弗化水素の濃度を増して10重量%を超えると、シリコ

ンウェハの表面に微粒子汚染物質が増加する傾向が認められる。また硝酸の濃度を増して25重量%を超えると、シリコン表面のエッチング量が過大になってウェハ表面が荒れて劣った状態になる。そして、弗化水素が10重量%以下でかつ硝酸が25重量%以下では、薬剤から混入する不純物の濃度は実質上問題ない。

したがって、弗化水素の濃度を0.1～20重量%、硝酸の濃度を0.5～25重量%とした。なお、洗浄温度については、必要以上に高温にすると弗化水素および水の蒸発や硝酸の蒸発分解が促進されて洗浄液の組成が本発明の範囲から外れるおそれがあり、さらに昇温に時間がかかり作業性を著しく損なうようになるので、90℃以下とするのが望ましい。

請求項(2)において、弗化水素が0.05重量%未

ンウェハの表面に微粒子汚染物質が増加するとともにエッチング量が過大になってウェハ表面が荒れる。そして、弗化水素が10重量%以下では薬剤から混入する不純物の濃度は実質上問題なく、また酸化性ガスは不純物濃度の極めて低い高純度のものが比較的容易に得られるので問題ない。

したがって、弗化水素の濃度を0.05～10重量%とし、酸化剤として酸化性ガスの気泡を混入せしめることとした。なお、洗浄温度については、80℃を超えると洗浄むらが生じて熱処理後のシリコンウェハ表面にピット状欠陥を誘起するおそれがあるので、80℃以下とするのが望ましい。

洗浄液に酸化性ガスの気泡を混入せしめるには、洗浄槽内にガス導入管を入れてバブリングさせるか、あるいは洗浄槽の底部にガス噴出孔を設けてバブリングさせる等の公知の手段を採用することができる。

本発明法によれば、シリコンと弗素イオンとの間に生じるシリコンのアノード溶解反応と、酸化剤の起こすカソード反応とが電気化学的にカップ

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ルして決められる腐食電位がアノード側になるので、シリコンウェハ表面の金属系汚染物質が除去されやすい。

本発明法の範囲の多量イオンを含む強酸性の水溶液中ではシリコン酸化物からなる不働態皮膜が化学的または電気化学的に溶解し、シリコンウェハ表面が元の状態になるため、酸化剤が必要量添加されて腐食電位がアノード側になるとウェハ表面の金属系汚染物質が容易に除去される。

なお、本発明法において、洗浄液の成分として上記以外のもの例えば希化アンモニウム等の塩類を洗浄液に添加したとしても洗浄能力が損なわれることがない。

さらに、本発明法において、従来公知の洗浄法と組み合わせてもよい。例えばアンモニアと過酸化水素の混合水溶液で洗浄し、さらに希硝酸水溶液で洗浄した後、本発明法により洗浄するとより効果的である。

実施例

(1) 請求項(1)の実施例

水性であるかを肉眼により判定し、疎水性であるものを○印、やや疎水性であるものを△印、親水性であるものを×印で表示した。疎水性であればシリコンウェハの表面にはシリコンの酸化物すなわち酸化膜が存在しないことを示す。

さらに、光学顕微鏡によりウェハ表面のピット状欠陥の有無を観察して表示した。ピット状欠陥なしは、エッチング量が適正で極めて平滑な鏡面状態の表面を有していることを示している。

第1表において、比較例のNo.1およびNo.15は希化水素が少ないため特にFeおよびCuの残存量が多く、同じくNo.8およびNo.14は希化水素が多すぎるためピット状欠陥が生じるとともに微粒子汚染物質が残存した。また、比較例のNo.19およびNo.20は炭酸が多すぎるためピット状欠陥が生じた。

従来例のNo.21 スライトエッチ法は HNO_3 :0.9重量％、 HF :0.1重量％の水溶液で洗浄したものであるがFeの除去効果が低い。No.22 アンモニア過酸化水素法は H_2O_2 :4.1重量％、 H_2O :4.4重量％の水

約 270×10^{10} atoms/cm² のCr、約 240×10^{10} atoms/cm² のCu、約 2230×10^{10} atoms/cm² のFeおよび約 312×10^{10} atoms/cm² のNiにより表面が汚染されたシリコンウェハを、第1表に示す各種洗浄液に被曝して洗浄した結果を同表に示す。洗浄後のシリコンウェハは、直ちに超純水中で5分間以上の流水水洗を2回行い、スピンドライヤーにより乾燥した後、表面の汚染金属の分析に供した。

分析は、過硝酸酸溶液によりシリコンウェハの表面1μmを化学エッチングして溶解し、被溶解液中の金属元素濃度をフレイムレス原子吸光光度分析法により定量した。なお、表中のNDは分析定量下限以下であることを示し、Crは 0.1×10^{10} atoms/cm² 未満、CuおよびFeは 0.2×10^{10} atoms/cm² 未満、Niは 2.0×10^{10} atoms/cm² 未満である。

ウェハ表面の微粒子は、ウェハ表面微粒子計測装置により測定し、10個/ウェハ以下を○印、10個/ウェハ面を×印で表示した。

また、洗浄後のウェハ表面が疎水性であるか親

水性で洗浄したもののであるが、各種洗浄法の中で最も金属系汚染物質の除去効果が低く、特にFeの除去効果が低い。No.23 希硝酸過酸化水素法は HNO_3 :0.1重量％、 H_2O_2 :4.4重量％の水溶液で洗浄したものであり、金属系汚染物質除去のために現在最も多用されている洗浄法であるが、本発明例に比べて特にFeの除去効果が低い。

本発明例(1)は、何れもシリコンウェハ表面の微粒子汚染物質および金属系汚染物質が極めて低減され、洗浄後の表面にピット状欠陥もない。また洗浄後の表面には酸化膜が存在せず、疎水性の表面状態になっている。これは、洗浄中に酸化膜が形成されてその中に洗浄液中の金属系汚染物質が取り込まれるという洗浄による再汚染が、本発明例(1)では生じていないことを意味する。

(2) 請求項(2)および請求項(3)の実施例

約 18×10^{10} atoms/cm² のCr、約 110×10^{10} atoms/cm² のCu、約 110×10^{10} atoms/cm² のFeおよび約 21×10^{10} atoms/cm² のNiにより表面が汚染されたシリコンウェハを、第2表に示す各種洗浄

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液に投致して洗浄した結果を同表に示す。洗浄後のシリコンウェハは実施例(1)と同様に水洗乾燥し、金属系汚染物質の分析、微粒子汚染物質の測定およびピット状欠陥の観察を行った。その結果を第2表に示す。

本発明の請求項(2)の実施例である本発明例(2)および請求項(3)の実施例である本発明例(3)は、何れも金属系汚染物質および微粒子汚染物質が極めて軽減され、かつピット状欠陥もない。

比較例のNo.8は弗化水素および過酸化水素が少ないため、また比較例のNo.9は弗化水素が少ないためCr、Cu、Feの残存量が多い。比較例のNo.15は酸化剤の量が少ないためCr、Cu、Feの残存量が多い。また、比較例のNo.16、No.17、No.19のように弗化水素や過酸化水素の量が多すぎると、ピット状欠陥が現れたり微粒子汚染物質が増加したりする。

第1表

No	HNO ₃ (%)	HF (%)	第三成分 (H ₂ O ₂)	洗浄時間 (秒)	温度 (℃)	洗浄後の表面汚染金属 (×10 ¹⁰ atoms/cm ²)				洗浄後の表面	ピット 状欠陥	微粒子 汚染	区 分
						Cr	Cu	Fe	Ni				
01	0.50	0.05	なし	300	25	81	2.3	23	ND	X	なし	○	比較例
02	0.10	0.10	なし	300	25	2.4	20	15	ND	△	なし	○	比較例
03	0.50	5.00	なし	300	25	ND	ND	ND	ND	○	なし	○	本発明例1
04	0.50	10.0	なし	300	25	ND	ND	ND	ND	○	なし	○	本発明例1
05	0.50	20.0	なし	300	25	ND	ND	ND	ND	○	なし	○	本発明例1
06	0.50	30.0	なし	300	25	ND	ND	ND	ND	○	あり	X	比較例
07	0.50	5.00	0.1%	300	25	ND	ND	ND	ND	○	なし	○	本発明例1
08	0.50	5.00	なし	300	40	ND	ND	ND	ND	○	なし	○	本発明例1
09	0.50	5.00	なし	300	60	ND	ND	ND	ND	○	なし	○	本発明例1
10	0.50	5.00	なし	300	80	ND	ND	ND	ND	○	なし	○	本発明例1
11	15.0	0.10	なし	300	25	ND	ND	ND	ND	○	なし	○	本発明例1
12	15.0	0.10	0.1%	300	25	ND	ND	ND	ND	○	なし	○	本発明例1
13	15.0	20.0	なし	300	25	ND	ND	ND	ND	○	なし	○	本発明例1
14	15.0	30.0	なし	300	25	ND	ND	ND	ND	○	あり	X	比較例
15	25.0	0.05	なし	300	25	ND	1.0	2.3	ND	X	なし	○	比較例
16	25.0	0.10	なし	300	25	ND	ND	ND	ND	○	なし	○	本発明例1
17	25.0	5.00	なし	300	25	ND	ND	ND	ND	○	なし	○	本発明例1
18	25.0	10.0	なし	300	25	ND	ND	ND	ND	○	なし	○	本発明例1
19	30.0	5.00	なし	300	25	ND	ND	ND	ND	○	あり	○	比較例
20	30.0	20.0	なし	300	25	ND	ND	ND	ND	○	あり	○	比較例
21	スライトエッチ法			300	20	ND	2.3	24	ND	X	なし	○	従来例
22	アンモニア過酸化水素法			600	80	2.7	2.4	77	ND	X	なし	○	従来例
23	硫酸過酸化水素法			600	80	ND	ND	15	ND	X	なし	○	従来例

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第 2 表

No	HF (%)	H ₂ O ₂ (%)	酸化性ガス の組成 (%)	第三成分	洗浄時間 (sec)	温度 (℃)	洗浄後表面金属 (×10 ¹⁰ atoms/cm ²)				ビット 状態	粒子 汚染	区 分
							Cr	Fe	Si	Cu			
01	6.05	1.00	なし	なし	800	25	ND	ND	ND	ND	なし	○	本発明例(2)
02	6.51	0.10	なし	なし	800	25	ND	ND	ND	ND	なし	○	本発明例(2)
03	6.19	2.01	なし	なし	800	25	ND	ND	ND	ND	なし	○	本発明例(2)
04	6.50	0.12	なし	なし	690	25	ND	ND	ND	ND	なし	○	本発明例(2)
05	1.05	0.11	なし	なし	300	25	ND	ND	ND	ND	なし	○	本発明例(2)
06	1.00	1.07	なし	NEAF 0.10%	240	25	ND	ND	ND	ND	なし	○	本発明例(2)
07	6.33	5.00	なし	なし	120	25	ND	ND	ND	ND	なし	○	本発明例(2)
08	6.63	6.04	なし	なし	600	25	4.2	6.8	ND	5.3	なし	○	比較例
09	6.01	1.04	なし	なし	600	25	13.2	20.4	ND	12.4	なし	○	比較例
10	6.10	0.29	なし	なし	800	40	ND	ND	ND	ND	なし	○	本発明例(2)
11	6.65	なし	pure O ₂	なし	600	25	ND	ND	ND	ND	なし	○	本発明例(3)
12	6.15	なし	80%O ₂ +20%Ar	なし	600	25	ND	ND	ND	ND	なし	○	本発明例(3)
13	1.01	なし	26%O ₂ +80%N ₂	NEAF 0.10%	300	20	ND	ND	ND	ND	なし	○	本発明例(3)
14	6.02	なし	pure O ₂	なし	300	25	5.8	45.0	ND	7.9	なし	○	比較例
15	6.15	0.01	なし	なし	600	25	6.8	12.8	ND	0.4	なし	○	比較例
16	11.0	2.05	なし	なし	600	25	ND	ND	ND	ND	なし	×	比較例
17	5.25	10.2	なし	なし	600	25	ND	ND	ND	ND	あり	○	比較例
18	11.2	なし	pure O ₂	なし	600	25	ND	ND	ND	ND	あり	×	比較例
19	1.00	なし	20%N ₂ O+80%N ₂	なし	800	30	ND	ND	ND	ND	なし	○	本発明例(2)

発明の効果

本発明法によりシリコンウェハを洗浄すると、金属系汚染物質および微粒子汚染物質がともに極めて低減された高純度のシリコンウェハが得られ、酸化誘起腐食欠陥の発生やライフタイムの低下といったシリコンウェハの品質低下が回避されるとともに、ICやLSIなどの高集積化したデバイスに使用した場合の電気特性劣化のおそれも回避される。

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(19) Japanese Patent Office (JP)
(12) Official Gazette for Unexamined Patent Applications (A)

(11) Japanese Patent Application Kokai Publication No. H03-208900

(43) Publication Date: September 12, 1991

Number of Claimed Inventions: 3 (total of 6 pages)

Request for Examination: Not requested

(51)	<u>International Class.⁵</u>	<u>Identification No.</u>	<u>JPO File No.</u>
	C 30 B 33/10		7158-4G

(54) Name of Invention: Cleaning Method for Silicon Wafer

(21) Application No.: H02-003386

(22) Application Date: January 12, 1990

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Specifications

1. Name of Invention

Cleaning Method for Silicon Wafer

2. Claims

(1) A method for cleaning a silicon wafer is characterized by a cleaning liquid comprised of an aqueous solution that contains 0.1 – 20 wt% hydrogen fluoride during the silicon wafer cleaning process, along with 0.5 – 25 wt% nitric acid that is used as an oxidizing agent.

(2) A method for cleaning a silicon wafer is further characterized by a cleaning liquid comprised of an aqueous solution that contains 0.05 – 10 wt% hydrogen fluoride during the silicon wafer cleaning process, along with 0.05 – 10 wt% hydrogen peroxide that is used as an oxidizing agent.

(3) A method for cleaning a silicon wafer is further characterized by a cleaning liquid comprised of an aqueous solution that contains 0.05 – 10 wt% hydrogen fluoride during the silicon wafer cleaning process, along with oxidizing gas bubbles that are mixed into the solution to be used as an oxidizing agent.

3. Detailed Description of the Invention

Industrial Field of Application

This invention pertains to a cleaning method designed to provide a high level of cleanliness along the surface of a silicon wafer.

Prior Art

In recent years, the high level of integration within devices has brought a strong demand for an improved level of cleanliness along the surface of the silicon wafers that are used as substrates for these devices.

When minute contaminants (also referred to as particles) exist along the surface of a silicon wafer, such as silicon particles, dust, etc., this can result in disconnections and shorts along the wires within a device, and in cases where metallic contaminants exist such as transition metals, other problems can arise such as the occurrence of defects along the oxidation inductive lamination layer, as well as a drop in the lifetime of the device. For this reason, when a cleaning process is conducted for the purpose of removing these contaminants, it is also necessary to prevent contamination during the cleaning process.

Recently, the following methods have been used for cleaning silicon wafers: (1) a method in which cleaning is conducted using a diluted hydrogen fluoride solution, (2) a method in which cleaning is conducted using a mixed solution of either hydrochloric acid or sulfuric acid and hydrogen peroxide, and (3) a method in which cleaning is conducted using a mixed solution of ammonia and hydrogen peroxide. The cleaning liquid used in each of these cleaning methods contains water and a highly pure form of chemicals designed to maximize the reduction of minute particle contaminants and transition metal contaminants.

Among the previous methods noted above, method (1) is capable of dissolving a natural oxide film with a normal thickness of 10Å on a silicon wafer surface, and while this method is highly effective at removing metallic contaminants within the oxide film, it still presents some difficulty when it comes to reducing the level of minute particle contaminants.

Method (2) is able to use a high level of dissolution capability with respect to the metallic contaminants contained within the sulfuric acid, but it is incapable of dissolving an oxide film. For this reason, it is highly effective when it comes to removing metallic contaminants located on top of an oxide film, but it has very little effect when it comes to removing metallic contaminants that are located within an oxide film or along the interface between an oxide film and silicon.

Since method (3) works to dissolve the silicon itself, it is highly effective at removing metallic contaminants located on top of the silicon layer. However, due to the fact that the oxide film that is generated within the basic cleaning solution can easily become embedded with the metallic contaminants, etc., that exist within the cleaning solution, there is a high possibility that the silicon wafer will become contaminated once again. However, due to the fact that this method is highly effective at removing minute particles, it is widely used among wafer manufacturers and device manufacturers.

In addition, as a method for resolving the problems experienced with the prior methods noted above, the so-called Slight Etch method was introduced in which a silicon wafer is cleaned by being dipped into a mixed solution of 60 wt% nitric acid and a maximum of 0.1 wt% hydrogen fluoride. (Ritsuo Takizawa, et al., "Extended Abstracts of Solid State Devices and Materials, 1988, P. 475)

However, highly pure nitric acid, which is referred to as semiconductor grade nitric acid, still contains ppb-order or sub-ppb-order metallic contaminants such as Al, Ca, Cu, Fe, K, Na, Zn, etc. Accordingly, there is a high concentration of metallic contaminants within cleaning solutions that contain a high concentration of nitric acid, such as 60 wt%. Furthermore, when a cleaning tank made of quartz glass is used, the metallic impurities within the quartz glass become eluted into the solution, causing the concentration to gradually increase.

Also, with the high oxidation strength of highly concentrated nitric acid, an oxide film forms on the surface of silicon wafers, and the metallic contaminants within the cleaning solution can easily become

embedded within this oxide film. Therefore, even when the Slight Etch method is applied, there is a limit to the level of high purification that takes place with regard to the silicon wafers.

Problem to Be Solved by the Invention

A method for evaluating the purity of silicon wafer surfaces is one in which the lifetime (hereinafter referred to as the recombination lifetime) is investigated using the microwave reflection method. Using this method, the inventors have evaluated the purity of silicon wafers that were cleaned according to each type of method available. The results showed that in cases where Fe is included in the cleaning solution during cleaning operations in which a mixed solution of ammonia and hydrogen peroxide is used, contamination occurs along the silicon wafer surface at a level of approximately 8×10^{11} atoms/cm² even when the Fe amount is very low at 0.5 ppb. It is further understood that this causes a drop in the recombination lifetime. (Otsuka, et al., The 34th Semiconductor and Integrated Circuit Technology Symposium, Preliminary Findings, 1988, P. 37)

The objectives of this invention are as follows: to significantly reduce the level of minute particle contaminants as well as metallic contaminants such as Fe when cleaning silicon wafers; to eliminate quality problems such as the occurrence of defects along the oxidation inductive lamination layer, as well as drops in lifetime; and to obtain a highly pure silicon wafer that will prevent degradation of electrical properties when used in devices.

An outline of this invention follows.

- (1) A method for cleaning a silicon wafer is characterized by a cleaning liquid comprised of an aqueous solution that contains 0.1 – 20 wt% hydrogen fluoride during the silicon wafer cleaning process, along with 0.5 – 25 wt% nitric acid that is used as an oxidizing agent.
- (2) A method for cleaning a silicon wafer is further characterized by a cleaning liquid comprised of an aqueous solution that contains 0.05 – 10 wt% hydrogen fluoride during the silicon wafer cleaning process, along with 0.05 – 10 wt% hydrogen peroxide that is used as an oxidizing agent.
- (3) A method for cleaning a silicon wafer is further characterized by a cleaning liquid comprised of an aqueous solution that contains 0.05 – 10 wt% hydrogen fluoride during the silicon wafer cleaning process, along with oxidizing gas bubbles that are mixed into the solution to be used as an oxidizing agent.

This invention is designed to minimize the amount of additives for the purpose of significantly reducing the level of impurities in a cleaning solution when a cleaning operation is conducted for silicon wafers. In addition, a cleaning solution with a superior level of cleaning capability is used. Specifically, this invention calls for an oxidizing agent to be added to a highly acidic aqueous solution containing a minimal amount of fluorine ions. Furthermore, as the oxide film along the silicon wafer surface is dissolved, an etching capability is provided for the silicon, making it possible to effectively remove metallic contaminants such as Fe, etc. Claim (1) notes that a minimal amount of nitric acid is used as an oxidizing agent, whereas Claim (2) notes that a minimal amount of hydrogen peroxide is used, and Claim (3) notes that an oxidizing gas is used.

According to this invention, the respective concentrations of hydrogen fluoride, nitric acid, and hydrogen peroxide within the cleaning solution are given in weight percentages of HF, HNO₃, and H₂O₂. In Claim (3), it is possible to use an oxidizing gas that contains oxygen as well as nitrous oxide (dinitrogen monoxide). Furthermore, an ultrapure form of water is used as a solvent.

In Claim (1), given less than 0.1 wt% of hydrogen fluoride and less than 0.5 wt% of nitric acid, the removal effect with regard to the metallic contaminants is insufficient. If the hydrogen fluoride concentration is increased to exceed 20 wt%, a trend is recognized in which the amount of minute particle contaminants increases along the surface of the silicon wafers. Furthermore, if the nitric acid concentration is increased to exceed 25 wt%, there is an excessive amount of etching along the silicon surface, resulting in a defective wafer surface with a cloudy appearance. Thus, if the maximum concentration of hydrogen fluoride is set to 20 wt% and the maximum concentration of nitric acid is set to 25 wt%, there is no substantial problem with regard to the concentration of impurities that become intermixed from the chemicals.

Therefore, the concentration of hydrogen fluoride has been set to a range of 0.1 – 20 wt%, and that of nitric acid has been set to a range of 0.5 – 25 wt%. Note that if the cleaning solution temperature is allowed to increase beyond the required level, this will cause the hydrogen fluoride as well as the water and nitric acid to escape in the form of steam and may result in a cleaning solution that falls outside the scope prescribed by the invention. Furthermore, increasing the temperature requires more time, which could result in a significant loss of productivity. Therefore, the preferred maximum temperature is 80°C.

In Claim (2), given less than 0.05 wt% of hydrogen fluoride and less than 0.05 wt% of hydrogen peroxide, the removal effect with regard to the metallic contaminants is insufficient. If the hydrogen fluoride concentration is increased to exceed 10 wt%, a trend is recognized in which the amount of minute particle contaminants increases along the surface of the silicon wafers. Furthermore, if the hydrogen peroxide concentration is increased to exceed 10 wt%, there is an excessive amount of etching along the silicon surface, resulting in a defective wafer surface with a cloudy appearance. Thus, if the maximum concentration of hydrogen fluoride is set to 10 wt% and the maximum concentration of hydrogen peroxide is set to 10 wt%, there is no substantial problem with regard to the concentration of impurities that become intermixed from the chemicals.

Therefore, the concentration of hydrogen fluoride has been set to a range of 0.05 – 10 wt%, and that of hydrogen peroxide has been set to a range of 0.05 – 10 wt%. Note that if the cleaning solution temperature is allowed to increase beyond 80°C, this will cause uneven cleaning such that pits may form on the silicon wafer surface after the heat treatment is conducted. Therefore, the preferred maximum temperature is 80°C.

In Claim (3), given less than 0.05 wt% of hydrogen fluoride and no intermixing of oxidizing gas bubbles, the removal effect with regard to the metallic contaminants is insufficient. If the hydrogen fluoride concentration is increased to exceed 10 wt%, the amount of minute particle contaminants increases along the surface of the silicon wafers, and at the same time, the etching amount becomes excessive, resulting in a defective wafer surface. Thus, if the maximum concentration of hydrogen fluoride is set to 10 wt%, there is no substantial problem with regard to the concentration of impurities that become intermixed from the chemicals. Furthermore, since a highly pure form of an oxidizing gas can be relatively easily obtained which has a very low concentration of impurities, this poses no problem.

Therefore, the concentration of hydrogen fluoride has been set to a range of 0.05 – 10 wt%, and oxidizing gas bubbles are intermixed to be used as an oxidizing agent. Note that if the cleaning solution temperature is allowed to increase beyond 80°C, this will cause uneven cleaning such that pits may form on the silicon wafer surface after the heat treatment is conducted. Therefore, the preferred maximum temperature is 80°C.

In order to intermix the oxidizing gas bubbles within the cleaning solution, it is possible to use a means that is already well-known, such as inserting a gas introduction tube into the cleaning tank or installing gas jets along the bottom of the cleaning tank such that the gas is allowed to bubble into the tank.

Based on this invention, there is an electrochemical coupling between the anodic dissolution reaction of the silicon that occurs between the silicon and fluorine ions, and the cathodic reaction that is caused by the oxidizing agent, resulting in a movement of the corrosion potential to the anode side. This makes it easy to remove the metallic contaminants from the silicon wafer surface.

Passive membranes comprised of silicon oxides are either chemically or electrochemically dissolved within the highly acidic aqueous solution containing fluorine ions that fall within the scope of the method discussed in this invention. Due to the fact that this will cause stripping of the silicon wafer surface, it is necessary to add a certain amount of oxidizing agent, and when the corrosion potential moves to the anode side, the metal contaminants are easily removed from the wafer surface.

Note that according to the method described in this invention, substances other than those noted above as components of the cleaning solution may also be added without causing a loss of cleaning capability. Examples include salt types such as ammonium fluoride, etc.

In addition, according to the method of this invention, it is also acceptable to use prior well-known forms of cleaning methods in conjunction with this method. As an example, for greater effect, cleaning can be conducted using a mixed solution of ammonia and hydrogen peroxide, followed by another cleaning in which a diluted fluorine aqueous solution is used, after which cleaning is finally conducted using the method of this invention.

Embodiments

<1> Embodiment for Claim 1

The surfaces of silicon wafers are contaminated with the following: approx. 270×10^{10} atoms/cm² of Cr, approx. 240×10^{10} atoms/cm² of Cu, approx. 2230×10^{10} atoms/cm² of Fe, and approx. 313×10^{10} atoms/cm² of Ni. These wafers are then dipped into the various cleaning solutions listed in Table 1, which provides the results for each cleaning. Immediately after cleaning, the silicon wafers are cleaned twice for at least five minutes each under ultrapure running water, after which they are spun dry and an analysis is conducted to determine the level of metallic contamination on the surface.

During the analysis, chemical etching using a concentrated fluorine and nitric acid solution is applied to dissolve a 1 μ m surface layer, after which the metallic element concentration within this solution is measured using a flameless atomic absorption photometry analysis method. Note that ND indicates a level that falls below the lower limit for analytical determination. Also note that Cr is less than 0.1×10^{10} atoms/cm², Cu and Fe are less than 0.2×10^{10} atoms/cm², and Ni is less than 2.0×10^{10} atoms/cm².

The minute particles on the wafer surface are measured using a wafer surface particulate measuring device, and those wafers showing 10 particulates per wafer or less are indicated with an O, whereas those showing more than 10 particulates per wafer are indicated with an X.

In addition, a visual judgment is made as to whether the wafer surfaces after cleaning are hydrophobic or hydrophilic. Those that are hydrophobic are indicated with an O, those that are slightly hydrophobic are marked with a Δ , and those that are hydrophilic are marked with an X. A hydrophobic surface indicates that a silicon oxide, namely an oxide layer, does not exist on the silicon wafer surface.

An optical microscope is then used in order to observe whether or not there are any pitting defects along the wafer surface, and the findings are included in the table. The absence of pits indicates that the etching amount is appropriate, such that the wafer has an extremely smooth mirror surface.

In Table 1, Comparison Examples 1 and 15 show that the residual amounts of Fe and Cu are particularly high due to the low levels of hydrogen fluoride during cleaning. In the same fashion, Comparison Examples 6 and 14 show a high occurrence of pitting as well as residual minute particle contamination due to the fact that the hydrogen fluoride levels are too high. Pitting defects also occur in the cases of Comparison Examples 19 and 20 due to the fact that the nitric oxide levels are too high.

Prior Art Example No. 21 in which the Slight Etch cleaning method is applied uses an aqueous solution that has 60 wt% of HNO_3 and 0.1 wt% of HF , but the removal effect is low with regard to Fe. Prior Art Example No. 22 in which the Ammonia Hydrogen Peroxide cleaning method is applied uses an aqueous solution that has 4.1 wt% of NH_3 and 4.4 wt% of H_2O_2 , and among the various cleaning methods, this one has the lowest removal effect with regard to metallic contaminants; especially in the case of Fe. Prior Art Example No. 23 in which the Chlorine Hydrogen Peroxide cleaning method is applied uses an aqueous solution that has 5.1 wt% of HCl and 4.4 wt% of H_2O_2 , and although this method is currently the most widely used due to its metallic contaminant removal effect, it still has a low removal effect with regard to Fe when compared to the examples given for this invention.

Example (1) of this invention shows a significant reduction in both minute particle contaminants as well as metallic contaminants, with no evidence of pitting defects on the surface after cleaning. Furthermore, the

surface is shown to be hydrophobic after cleaning, with no existence of an oxide film. This means that the type of recontamination that occurs when cleaning is performed in such a way that an oxide film is formed during cleaning and metallic contaminants within the cleaning solution are allowed to become embedded within the oxide film has not occurred in the case of Example 1 of this invention.

<2> Embodiments for Claims 2 and 3

The surfaces of silicon wafers are contaminated with the following: approx. 18×10^{10} atoms/cm² of Cr, approx. 110×10^{10} atoms/cm² of Cu, approx. 110×10^{10} atoms/cm² of Fe, and approx. 21×10^{10} atoms/cm² of Ni. These wafers are then dipped into the various cleaning solutions listed in Table 2, which provides the results for each cleaning. The cleaned wafers then undergo the same procedures as noted in Embodiment <1> with regard to water rinsing and drying, followed by an analysis of the metallic contaminants, measurements regarding minute particle contaminants, and observations of pitting defects. The results are shown in Table 2.

Examples (2) and (3) of this invention, which are the respective embodiments of Claims (2) and (3) of this invention, show that the levels of metallic contaminants and minute particle contaminants are drastically reduced, with no evidence of pitting defects.

Due to the low levels of hydrogen fluoride and hydrogen peroxide used during cleaning in the case of Comparison Example No. 8, as well as the low level of hydrogen fluoride used during cleaning in the case of Comparison Example No. 9, both of these examples show high residual amounts of Cr, Cu, and Fe. In the case of Comparison Example No. 15, the low level of oxidizing agent used during cleaning results in high residual amounts of Cr, Cu, and Fe. Also, as shown in Comparison Examples No. 16, No. 17, and No. 18, excessive amounts of hydrogen fluoride and hydrogen peroxide result in the appearance of pitting defects as well as an increase in the level of minute particle contaminants.

Table 1

No.	HNO ₃ (%)	HF (%)	Third Com- po- nent (NH ₄ F)	Clean- ing Time (sec.)	Sol. Temp. (°C)	Heavy metal contamination on Surface after cleaning ($\times 10^{10}$ atoms/cm ²)				Surface After Cleaning	Pitting Defects	Min. Part. Cont.	Class.
						Cr	Cu	Fe	Ni				
01	0.50	0.05	None	300	25	61	2.3	23	ND	X	None	O	CE
02	0.10	0.10	None	300	25	2.4	20	15	ND	Δ	None	O	CE
03	0.50	5.00	None	300	25	ND	ND	ND	ND	O	None	O	PE1
04	0.50	10.0	None	300	25	ND	ND	ND	ND	O	None	O	PE1
05	0.50	20.0	None	300	25	ND	ND	ND	ND	O	None	O	PE1
06	0.50	30.0	None	300	25	ND	ND	ND	ND	O	Yes	X	CE
07	0.50	5.00	0.1%	300	25	ND	ND	ND	ND	O	None	O	PE1
08	0.50	5.00	None	300	40	ND	ND	ND	ND	O	None	O	PE1
09	0.50	5.00	None	300	60	ND	ND	ND	ND	O	None	O	PE1
10	0.50	5.00	None	300	80	ND	ND	ND	ND	O	None	O	PE1
11	15.0	0.10	None	300	25	ND	ND	ND	ND	O	None	O	PE1
12	15.0	0.10	0.1%	300	25	ND	ND	ND	ND	O	None	O	PE1

13	15.0	20.0	None	300	25	ND	ND	ND	ND	O	None	O	PE1
14	15.0	30.0	None	300	25	ND	ND	ND	ND	O	Yes	X	CE
15	25.0	0.05	None	300	25	ND	1.8	3.3	ND	X	None	O	CE
16	25.0	0.10	None	300	25	ND	ND	ND	ND	O	None	O	PE1
17	25.0	5.00	None	300	25	ND	ND	ND	ND	O	None	O	PE1
18	25.0	10.0	None	300	25	ND	ND	ND	ND	O	None	O	PE1
19	30.0	5.00	None	300	25	ND	ND	ND	ND	O	Yes	O	CE
20	30.0	20.0	None	300	25	ND	ND	ND	ND	O	Yes	O	CE
21	Slight Etch Method			300	70	ND	2.8	34	ND	X	None	O	PAE
22	Ammonia Hydrogen Peroxide Method			600	80	2.7	2.4	77	ND	X	None	O	PAE
23	Chlorine Hydrogen Peroxide Method			600	80	ND	ND	15	ND	X	None	O	PAE

[Translator's Note: In the Classification (Class.) column above, CE = Comparison Example; PE1 = Patent Example (1); PAE = Prior Art Example]

Table 2

No.	HF (%)	H ₂ O ₂ (%)	Oxidiz- ing Gas Com- posi- tion (%)	Third Com- po- nent	Clean- ing Time (sec.)	Sol. Temp. (°C)	Heavy metal contamination on Surface after cleaning (x 10 ¹⁰ atoms/cm ²)				Pitting Defects	Min. Part. Cont.	Class.
							Cr	Fe	Ni	Cu			
01	0.05	1.00	None	None	600	25	ND	ND	ND	ND	None	O	PE2
02	0.51	0.10	None	None	600	25	ND	ND	ND	ND	None	O	PE2
03	0.10	2.01	None	None	600	25	ND	ND	ND	ND	None	O	PE2
04	0.50	0.12	None	None	600	25	ND	ND	ND	ND	None	O	PE2
05	1.05	0.11	None	None	360	25	ND	ND	ND	ND	None	O	PE2
06	1.00	1.07	None	NH ₄ F 0.10%	240	25	ND	ND	ND	ND	None	O	PE2
07	0.99	5.00	None	None	120	25	ND	ND	ND	ND	None	O	PE2
08	0.03	0.04	None	None	600	25	8.2	6.8	ND	5.3	None	O	CE
09	0.01	1.00	None	None	600	25	ND	23.4	ND	12.4	None	O	CE
10	0.10	0.20	None	None	600	40	ND	ND	ND	ND	None	O	PE2
11	0.05	None	Pure O ₂	None	600	25	ND	ND	ND	ND	None	O	PE3
12	0.15	None	80%O ₂ + 20%Ar	None	600	25	ND	ND	ND	ND	None	O	PE3
13	1.01	None	20%O ₂ +80%N ₂	NH ₄ F 0.10%	360	30	ND	ND	ND	ND	None	O	PE3
14	0.02	None	Pure O ₂	None	360	25	ND	45.8	ND	7.9	None	O	CE
15	0.15	0.01	None	None	600	25	ND	12.4	ND	8.4	None	O	CE
16	11.0	2.05	None	None	600	25	ND	ND	ND	ND	None	X	CE
17	5.95	10.2	None	None	600	25	ND	ND	ND	ND	Yes	O	CE
18	11.2	None	Pure O ₂	None	600	25	ND	ND	ND	ND	Yes	X	CE
19	1.00	None	20%N ₂ O + 80%N ₂	None	600	30	ND	ND	ND	ND	None	O	PE3

[Translator's Note: In the Classification (Class.) column above, CE = Comparison Example; PE2 = Patent Example (2); PE3 = Patent Example (3)]

Effect of the Invention

When a silicon wafer is cleaned using the method described in this invention, a highly pure silicon wafer can be obtained in which the levels of metallic contaminants and minute particle contaminants are significantly reduced. Furthermore, not only does this invention make it possible to avoid a drop in quality among silicon wafers, such as the occurrence of defects along the oxidation inductive lamination layer as well as a drop in lifetime, when these wafers are used in highly integrated devices such as IC, LSI, etc., it is also possible to prevent degradation of electrical properties in these devices.

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